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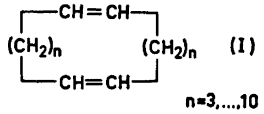
Crystal Conformation of *cis,cis*-1,2,11,12-Tetrakis-trimethylsiloxycycloeikosadien-1,11 at −160 °C

P. GROTH

Department of Chemistry, University of Oslo, Oslo 3, Norway

The crystals of $C_{32}H_{68}O_4Si_4$ belong to the monoclinic system with space group $P2_1/n$, cell dimensions $a = 8.439(3)$ Å, $b = 26.909(16)$ Å, $c = 17.326(8)$ Å, $\beta = 96.70(4)°$, and four molecules in the unit cell. The structure was solved by direct methods and refined by full-matrix least-squares technique to a final weighted R-value of 5.1 % (conventional $R = 5.9$ %) for 3464 observed reflections collected at −160 °C on an automatic four circle X-ray diffractometer. The conformation of the 20-membered ring may be described in terms of a pseudo two-fold axis of rotation and two "corner" atoms. Two additional "corners" are created by the *cis* double bonds.

The thermodynamic equilibria between the *trans,trans*-, *cis,trans*-, and *cis,cis*-isomers of symmetrical cycloalkadienes with the general formula I have been studied by Dale and



(I)

Moussebois.[1] For $n = 5$, 7 and 9 there are strong preferences for the *trans,trans*-isomers, while no

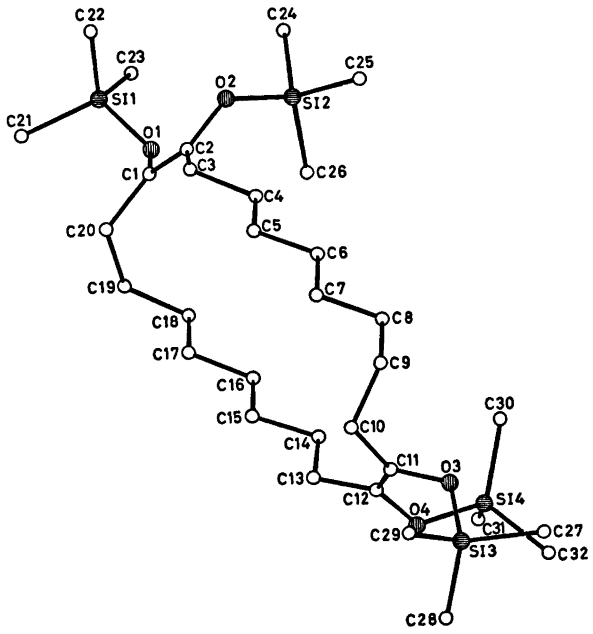


Fig. 1. Schematic drawing of the molecule.

such effects are observed for the 16- and 20-membered rings ($n=6$ and 8). In order to obtain detailed conformational information, the crystal structure of *cis,cis*-1,2,11,12-tetrakistrimethylsiloxycycloeikosadien-1,11, illustrating the case $n=8$, has been determined.

The crystals of $C_{32}H_{68}O_4Si_4$ belong to the monoclinic system with space group $P2_1/n$, cell dimensions $a=8.439(3)$ Å, $b=26.909(16)$ Å, $c=17.326(8)$ Å, $\beta=96.70(4)°$, and $Z=4$ ($D_m=1.04$ g cm^{-3}, $D_x=1.06$ g cm^{-3}). Data were collected at -160 °C on an automatic four circle

Table 1. Final fractional coordinates and thermal parameters with estimated standard deviations. The expression for anisotropic vibration is $\exp[-2\pi^2(h^2a^{*2}U11+\cdots+2klb^*c^*U23)]$. Hmn is bonded to Cm.

ATOM	X	Y	Z	U11	U22	U33	U12	U13	U23
SI1	.38421(16)	.45286(6)	.88384(9)	.0296(7)	.0193(9)	.0153(9)	-.0024(7)	-.0037(6)	.0008(7)
SI2	.27667(17)	.60428(6)	.17773(9)	.0343(7)	.0177(9)	.0225(10)	.0049(7)	-.0063(7)	-.0007(6)
SI3	1.21868(16)	.72757(6)	.79438(9)	.0278(7)	.0281(9)	.0201(10)	.0018(7)	-.0064(7)	-.0036(6)
SI4	1.21863(16)	.74785(6)	.64269(9)	.0293(7)	.0192(9)	.0225(9)	-.0039(7)	-.0025(6)	.0042(6)
O1	.42152(35)	.49249(12)	.13690(19)	.0317(17)	.0242(22)	.0162(21)	-.0011(15)	-.0014(15)	.0018(17)
O2	.28775(36)	.55225(12)	.22791(19)	.0288(17)	.0216(21)	.0288(24)	.0021(16)	-.0017(16)	-.0019(18)
O3	1.09412(35)	.71972(12)	.71287(19)	.0324(16)	.0202(21)	.0198(23)	.0008(15)	-.0028(15)	-.0043(18)
O4	1.25105(37)	.69307(12)	.58836(20)	.0335(18)	.0188(21)	.0263(22)	-.0012(16)	.0011(16)	.0032(18)
C1	.48362(55)	.49048(18)	.21854(29)	.0282(25)	.0196(31)	.0161(33)	-.0025(23)	-.0031(23)	.0022(26)
C2	.37474(56)	.52824(18)	.26155(29)	.0245(24)	.0166(31)	.0284(35)	-.0038(23)	-.0033(23)	.0036(26)
C3	.39540(54)	.58268(19)	.34892(29)	.0288(25)	.0277(35)	.0200(33)	.0019(24)	.0010(23)	-.0024(27)
C4	.48741(56)	.57313(21)	.38143(31)	.0339(27)	.0373(38)	.0208(34)	.0029(26)	.0012(24)	-.0011(29)
C5	.81488(55)	.57991(20)	.46859(31)	.0306(26)	.0239(34)	.0295(37)	-.0009(24)	.0005(25)	.0016(29)
C6	.86711(54)	.62879(19)	.50148(28)	.0324(26)	.0263(35)	.0167(32)	.0003(24)	-.0033(23)	-.0011(26)
C7	.84184(55)	.61869(20)	.58685(30)	.0327(26)	.0323(37)	.0194(33)	-.0097(25)	-.0027(24)	.0019(28)
C8	.89713(58)	.66999(20)	.61848(31)	.0346(27)	.0266(37)	.0247(36)	-.0016(25)	-.0034(24)	-.0002(29)
C9	.77985(57)	.66789(20)	.70153(30)	.0319(26)	.0336(36)	.0284(34)	-.0022(26)	.0022(24)	-.0038(28)
C10	.94242(56)	.64297(20)	.71864(30)	.0312(27)	.0336(37)	.0168(33)	-.0024(25)	-.0045(23)	-.0031(28)
C11	1.06869(52)	.67324(20)	.67710(30)	.0256(25)	.0237(35)	.0196(33)	.0041(23)	.0006(24)	-.0001(28)
C12	1.14298(53)	.66150(18)	.61671(30)	.0274(25)	.0166(31)	.0269(36)	.0009(23)	-.0047(25)	.0062(26)
C13	1.12711(53)	.61322(18)	.57211(29)	.0328(25)	.0176(33)	.0244(33)	-.0017(23)	.0062(24)	.0018(26)
C14	1.05155(56)	.61731(20)	.48748(30)	.0370(27)	.0277(36)	.0196(33)	-.0035(25)	.0009(24)	-.0011(27)
C15	1.08664(55)	.56656(19)	.45238(30)	.0328(26)	.0177(33)	.0265(35)	-.0007(23)	.0018(24)	-.0021(27)
C16	.94186(56)	.56767(20)	.36554(31)	.0344(27)	.0264(35)	.0248(35)	.0046(24)	.0025(24)	.0003(27)
C17	.88072(55)	.51771(20)	.33521(30)	.0312(26)	.0223(34)	.0265(35)	-.0018(24)	-.0042(24)	.0058(28)
C18	.81623(54)	.51853(19)	.24943(30)	.0297(25)	.0243(33)	.0223(34)	-.0022(23)	.0034(23)	.0026(27)
C19	.74573(57)	.46864(19)	.21882(30)	.0340(27)	.0251(34)	.0217(34)	.0078(24)	-.0019(25)	.0013(27)
C20	.58645(54)	.45508(20)	.24783(29)	.0313(25)	.0254(33)	.0186(32)	-.0019(24)	-.0003(23)	-.0013(27)
C21	.11174(72)	.44731(24)	.12491(34)	.0624(37)	.0498(44)	.0322(40)	-.0153(34)	-.0031(31)	-.0018(34)
C22	.39863(75)	.39059(23)	.86987(36)	.0728(38)	.0393(41)	.0388(42)	.0891(34)	-.0246(34)	-.0145(34)
C23	.27737(59)	.47843(21)	-.01691(31)	.0370(28)	.0386(38)	.0281(36)	.0018(26)	.0015(26)	-.0041(29)
C24	.13662(74)	.59884(23)	.88673(37)	.0714(39)	.0361(41)	.0474(44)	.0886(34)	-.0239(35)	.0845(35)
C25	.48819(66)	.61488(21)	.15787(35)	.0562(34)	.0295(36)	.0455(42)	.0182(29)	.0088(31)	-.0056(33)
C26	.21149(63)	.65742(20)	.23486(34)	.0485(32)	.0265(37)	.0426(42)	.0843(27)	-.0033(29)	.0007(31)
C27	1.16363(68)	.68665(21)	.87362(32)	.0391(28)	.0393(39)	.0277(37)	-.0007(27)	-.0065(26)	-.0001(30)
C28	1.42538(61)	.71428(21)	.77642(34)	.0391(29)	.0383(39)	.0307(40)	-.0010(27)	-.0083(28)	-.0085(32)
C29	1.18981(67)	.79352(22)	.82153(34)	.0542(34)	.0431(42)	.0343(38)	.0043(30)	-.0068(30)	-.0113(33)
C30	1.29218(68)	.74165(21)	.44698(34)	.0555(32)	.0341(39)	.0378(40)	.0846(30)	.0083(29)	.0088(33)
C31	1.88088(68)	.76681(19)	.52954(31)	.0445(29)	.0236(35)	.0281(35)	-.0892(25)	-.0064(26)	.0129(28)
C32	1.33188(63)	.79658(20)	.89981(35)	.0468(31)	.0190(35)	.0513(43)	-.0070(27)	-.0052(30)	.0091(31)

ATOM	X	Y	Z	B	ATOM	X	Y	Z	B
H31	.4832(46)	.4967(16)	.3683(24)	.8(9)	H32	.2907(48)	.5143(16)	.3662(25)	.4(9)
H41	.3597(62)	.5006(20)	.3657(32)	4.6(14)	H42	.5475(49)	.5798(16)	.3539(26)	1.8(10)
H81	.6019(49)	.5452(17)	.4775(26)	1.4(10)	H82	.4281(56)	.5591(19)	.4946(28)	2.2(12)
H61	.4776(59)	.6442(17)	.4966(26)	1.8(10)	H62	.6572(48)	.6355(16)	.4728(25)	1.8(10)
H71	.7425(48)	.6018(17)	.5857(26)	1.8(10)	H72	.5617(59)	.6028(19)	.6159(29)	2.4(12)
H81	.8976(58)	.6923(17)	.6118(25)	.9(10)	H82	.7692(53)	.6849(18)	.5846(27)	2.5(11)
H91	.7158(49)	.6512(16)	.7378(26)	1.5(10)	H92	.7867(46)	.7882(15)	.7266(24)	1.7(9)
H101	.9318(58)	.6892(17)	.6876(26)	1.5(10)	H102	.9817(59)	.6374(19)	.7670(30)	3.8(13)
H131	1.0878(49)	.5876(16)	.6823(25)	.6(10)	H132	1.2322(47)	.6818(16)	.5721(25)	1.3(9)
H141	1.1288(52)	.6362(18)	.4579(27)	1.8(11)	H142	.9483(57)	.6373(19)	.4865(29)	2.8(12)
H151	.9294(54)	.5534(19)	.4846(28)	1.9(11)	H152	1.1895(49)	.5483(17)	.4680(26)	1.8(10)
H161	1.0279(44)	.5788(15)	.3354(24)	1.0(9)	H162	.8647(47)	.5896(16)	.3601(25)	.6(10)
H171	.7808(51)	.5868(17)	.3655(27)	2.5(10)	H172	.9724(49)	.4981(16)	.3468(26)	1.7(10)
H181	.9029(49)	.5289(16)	.2202(26)	.6(10)	H182	.7163(62)	.5437(19)	.2429(31)	3.4(13)
H191	.8273(57)	.4426(18)	.2339(30)	2.5(12)	H192	.7485(57)	.4780(18)	.1631(30)	3.0(12)
H201	.5902(44)	.4498(15)	.3065(24)	.4(9)	H202	.5602(54)	.4213(17)	.2291(28)	2.4(11)
H211	.0606(49)	.4796(17)	.1251(26)	1.8(10)	H212	.0373(72)	.4158(21)	.0996(34)	5.9(16)
H213	.1239(70)	.4398(23)	.1757(34)	6.1(16)	H221	.5073(51)	.3956(17)	.8702(27)	2.4(10)
H222	.3512(64)	.3671(25)	.9464(40)	7.2(19)	H223	.4029(54)	.3775(18)	.1302(28)	2.3(11)
H231	.2311(68)	.5108(20)	-.0172(31)	2.4(13)	H232	.3713(63)	.4883(20)	-.0341(33)	3.7(13)
H233	.2132(66)	.4568(21)	-.0466(32)	4.8(15)	H241	.8336(54)	.5959(18)	.1027(27)	4.2(11)
H242	.1299(64)	.6282(21)	.8586(32)	4.3(14)	H243	.1738(78)	.5758(24)	.0553(38)	7.5(18)
H251	.5215(52)	.5887(17)	.1271(27)	1.9(11)	H252	.5478(63)	.6212(20)	.2044(32)	4.8(13)
H253	.4803(66)	.6476(21)	.1298(34)	4.2(15)	H261	.1859(58)	.6556(17)	.2416(26)	2.3(11)
H262	.2951(74)	.6652(23)	.2782(38)	5.2(17)	H263	.2381(68)	.6898(21)	.2895(34)	3.7(14)
H271	1.0583(61)	.6846(20)	.8785(32)	2.4(13)	H272	1.1931(65)	.6532(21)	.8644(33)	2.4(14)
H273	1.2399(53)	.6966(18)	.9215(27)	2.5(11)	H281	1.5813(57)	.7148(19)	.8249(29)	5.1(12)
H282	1.4723(46)	.7365(16)	.7431(25)	3.7(9)	H283	1.4329(54)	.6811(17)	.7529(28)	3.3(11)
H291	1.2253(55)	.8114(18)	.7805(29)	2.6(11)	H292	1.0874(62)	.7979(20)	.8283(31)	2.2(13)
H293	1.2581(68)	.8001(22)	.8707(34)	5.8(15)	H301	1.4111(48)	.7329(16)	.4551(26)	4.9(10)
H302	1.2399(56)	.7155(18)	.4115(29)	4.7(11)	H303	1.2657(53)	.7732(18)	.4188(28)	3.2(11)
H311	.9327(64)	.7360(20)	.4962(33)	3.7(14)	H312	.9462(57)	.7612(19)	.5804(29)	.4(12)
H313	.9933(53)	.7896(18)	.5091(28)	2.1(11)	H321	1.2769(54)	.8002(17)	.6463(28)	3.8(11)
H322	1.4453(52)	.7877(17)	.6021(27)	4.9(11)	H323	1.3298(77)	.8288(23)	.5729(37)	3.3(16)

Table 2. Bond distances, bond angles and dihedral angles with estimated standard deviations

DISTANCE	(Å)	DISTANCE	(Å)
SI1 - O1	1.659(3)	SI2 - O2	1.663(4)
SI3 - O3	1.662(3)	SI4 - O4	1.662(4)
SI1 - C21	1.854(6)	SI1 - C22	1.857(6)
SI1 - C23	1.852(6)	SI2 - C24	1.860(6)
SI2 - C25	1.856(6)	SI2 - C26	1.858(6)
SI3 - C27	1.858(6)	SI3 - C28	1.859(6)
SI3 - C29	1.857(6)	SI4 - C30	1.853(6)
SI4 - C31	1.848(5)	SI4 - C32	1.855(6)
O1 - C1	1.410(6)	O2 - C2	1.386(6)
O3 - C11	1.402(6)	O4 - C12	1.387(6)
C1 - C2	1.326(7)	C11 - C12	1.319(7)
C2 - C3	1.505(7)	C3 - C4	1.538(7)
C4 - C5	1.532(7)	C5 - C6	1.505(7)
C6 - C7	1.548(7)	C7 - C8	1.538(7)
C8 - C9	1.524(7)	C9 - C10	1.528(7)
C10 - C11	1.507(7)	C12 - C13	1.509(7)
C13 - C14	1.533(7)	C14 - C15	1.525(7)
C15 - C16	1.542(7)	C16 - C17	1.510(7)
C17 - C18	1.522(7)	C18 - C19	1.538(7)
C19 - C20	1.528(7)	C20 - C1	1.509(7)

ANGLE	(°)	ANGLE	(°)
O1 - SI1 - C21	109.4(2)	O1 - SI1 - C22	111.5(2)
O1 - SI1 - C23	106.1(2)	C21 - SI1 - C22	109.7(3)
C21 - SI1 - C23	111.8(3)	C22 - SI1 - C23	108.4(3)
O2 - SI2 - C24	106.8(2)	O2 - SI2 - C25	111.4(2)
O2 - SI2 - C26	108.6(2)	C24 - SI2 - C25	112.0(3)
C24 - SI2 - C26	108.4(3)	C25 - SI2 - C26	109.4(3)
O3 - SI3 - C27	111.8(2)	O3 - SI3 - C28	110.8(2)
O3 - SI3 - C29	104.8(2)	C27 - SI3 - C28	109.0(3)
C27 - SI3 - C29	109.3(3)	C28 - SI3 - C29	111.9(3)
O4 - SI4 - C30	107.2(2)	O4 - SI4 - C31	110.7(2)
O4 - SI4 - C32	109.8(2)	C30 - SI4 - C31	109.9(3)
C30 - SI4 - C32	108.3(3)	C31 - SI4 - C32	111.6(3)
SI1 - O1 - C1	124.2(3)	SI2 - O2 - C2	129.6(3)
SI3 - O3 - C11	122.6(3)	SI4 - O4 - C12	127.8(3)
O1 - C1 - C20	113.7(4)	O1 - C1 - C2	119.3(4)
C20 - C1 - C2	126.9(5)	O2 - C2 - C1	121.3(4)
O2 - C2 - C3	112.9(4)	C1 - C2 - C3	125.7(4)
O3 - C11 - C10	113.1(4)	O3 - C11 - C12	120.0(5)
C10 - C11 - C12	126.7(5)	O4 - C12 - C11	122.2(5)
O4 - C12 - C13	111.5(4)	C11 - C12 - C13	126.3(5)
C2 - C3 - C4	113.7(4)	C3 - C4 - C5	112.4(5)
C4 - C5 - C6	112.5(5)	C5 - C6 - C7	113.6(4)
C6 - C7 - C8	112.5(4)	C7 - C8 - C9	112.9(5)
C8 - C9 - C10	114.9(5)	C9 - C10 - C11	113.0(4)
C12 - C13 - C14	115.4(4)	C13 - C14 - C15	111.9(4)
C14 - C15 - C16	114.6(4)	C15 - C16 - C17	113.0(4)
C16 - C17 - C18	113.2(5)	C17 - C18 - C19	113.8(4)
C18 - C19 - C20	114.8(5)	C19 - C20 - C1	113.0(4)

DIHEDRAL ANGLE	(°)
C1 - C2 - C3 - C4	116.7(6)
C2 - C3 - C4 - C5	-166.5(4)
C3 - C4 - C5 - C6	-177.0(4)
C4 - C5 - C6 - C7	-173.9(4)
C5 - C6 - C7 - C8	178.9(4)
C6 - C7 - C8 - C9	-176.8(4)
C7 - C8 - C9 - C10	69.7(6)
C8 - C9 - C10 - C11	78.1(6)
C9 - C10 - C11 - C12	-113.7(6)
C10 - C11 - C12 - C13	-5.4(8)
C11 - C12 - C13 - C14	114.7(6)
C12 - C13 - C14 - C15	-167.3(4)
C13 - C14 - C15 - C16	-175.8(4)
C14 - C15 - C16 - C17	-173.5(4)
C15 - C16 - C17 - C18	-179.8(4)
C16 - C17 - C18 - C19	-176.8(4)
C17 - C18 - C19 - C20	71.9(5)
C18 - C19 - C20 - C1	64.5(6)
C19 - C20 - C1 - C2	-115.6(6)
C20 - C1 - C2 - C3	-3.8(8)

diffractometer (MoK_α-radiation). Using an observed-unobserved cutoff at $2\sigma(I)$, 3464 reflections were recorded as observed. No corrections for absorption or secondary extinction were applied (crystal size $0.3 \times 0.2 \times 0.3$ mm [3]).

The structure was solved by direct methods [2] and refined by full-matrix least-squares technique.[3*] The positions of methylene hydrogen atoms were calculated while those of the methyl groups were localized in a difference Fourier map. Anisotropic temperature factors were introduced for Si, O and C atoms and weights in least squares were calculated from the standard deviations in intensities, $\sigma(I)$, taken as

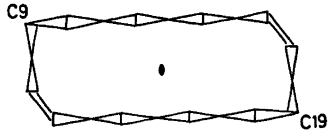
$$\sigma(I) = [C_T + (0.02C_N)^2]^{\frac{1}{2}}$$

where C_T is the total number of counts and C_N the net count. The final weighted R-value was 5.1 % (conventional $R = 5.9$ %) for 3464 observed reflections. The form factors used were those of Hanson *et al.*[4] except for hydrogen.[5]

Final fractional coordinates and thermal parameters are given in Table 1. The principal axes of thermal vibration ellipsoids were calculated from the temperature parameters of this table, and the maximum r.m.s. amplitudes range from 0.175 to 0.316 Å (corresponding B-values 2.42 and 7.88 Å^2). Due to the size of the molecule no rigid-body analysis has been carried out.

Bond distances and angles and dihedral angles are listed in Table 2. Fig. 1 is a schematic drawing of the molecule indicating the numbering of atoms.

The conformation of the 20-membered ring may be described in terms of a pseudo two-fold axis of rotation (approximately parallel to [01$\bar{1}$] and two "corner" atoms (C9 and C19):



Two additional corners are effectively created by the *cis* double bonds.

The average Si – O bond distance of 1.662 Å seems to be somewhat longer than that of 17β-trimethylsiloxy-4-androsten-3-one (silandrone)[6] [1.623(7) Å]. Within error limits the Si – C bond length (mean value 1.856 Å) agrees with the corresponding value of silandrone [1.87(1) Å] and with the more accurate average Si – C bond distance in 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane [7] of 1.851 Å. C – C bond lengths

* All programs used (except those for phase determination) are included in this reference.

and bond angles have normal values. The only short H–H contacts are H31···H201 (1.94 Å) and H101···H131 (2.06 Å).

A list of observed and calculated structure factors is available from the author.

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